Development of a Gas and Particulate Matter Organic Speciation Profile Database

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1.0 Background

The purpose of the California Regional $PM_{10}/PM_{2.5}$ Air Quality Study (CRPAQS) is to improve current scientific understanding of excessive PM levels in central California (Watson et al., 1998a). CRPAQS is an integrated effort that includes air quality and meteorological field measurements, emissions characterization, data analysis, and air quality modeling. CRPAQS activities are complementary to long-term monitoring and research activities being conducted by the California Air Resources Board (ARB), the U.S. Environmental Protection Agency (EPA), the San Joaquin Valley Unified Air Pollution Control District (SJVUAPCD), the Bay Area Air Quality Management District (BAAQMD), the Great Basin Air Pollution Control District (GBAPCD), and other air quality districts in the region. The specific objectives of the CRPAQS are to:

- Provide an improved understanding of emission and dynamic atmospheric processes that influence particle formation and distribution.

- Develop and demonstrate methods useful to decision makers in formulating and comparing candidate control strategies for attaining the federal and state PM_{10} and $PM_{2.5}$ standards in central California.

- Provide reliable means for estimating the impacts of control strategy options developed for $PM_{10}/PM_{2.5}$ on visibility, air toxics, and acidic aerosols and on attainment strategies for other regulated pollutants, notably ozone.

One of the major objectives of CRPAQS is to determine the contributions of various source categories to episodic levels of suspended particles. The episodes of highest PM_{10} concentrations are generally found in the wintertime during stagnation conditions. The receptor modeling approach generally used to determine source contributions requires accurate and precise measurements of the chemical composition of PM_{10} or $PM_{2.5}$ emissions from sources that are likely to contribute to high ambient PM concentrations. The chemical mass balance approach (CMB) can be applied to an ambient particulate sample after chemical speciation to determine the significance of various sources in the sample.

The more distinct the chemical profile of a source, the more accurately CMB can be used to determine source contribution. Sources that contain one or a few compounds are difficult to differentiate from other sources. The chemical profiles of soil-derived particulate matter contain primarily silicon, aluminum, and iron regardless of the origin (unpaved roads, disturbed land, paved roads), and thus it is difficult to distinguish the contribution of each source. By contrast, particles that contain significant amounts of organic carbon usually consist of hundreds of different compounds, and the compositions of these sources often are unique to the formation. Carbonaceous material also has been shown to account for 30% to 37% of the $PM_{2.5}$ mass in urban areas of the San Joaquin Valley (Watson et al., 1997). Quantifying the organic constituents of such particulate matter can be useful in applying CMB to determine the magnitude of a specific source if the source profile is known.

2.0 Objective

The objective of this project was to determine the chemical content of sources that are needed to perform the CMB modeling using ambient particulate composition in order to meet the CRPAQS objective of determining the contributions of these sources to the PM concentrations in the San Joaquin Valley. The database generated includes chemical speciation of the gaseous, semi-volatile, and particulate species for each source.

3.0 Approach

Our approach began with the selection of sources for which chemical speciation was needed to improve CMB determination of source contributions in the San Joaquin Valley. The sources and modes of operation were chosen to be representative of those in the Valley. The significance of sources to the total PM burden is difficult to determine because source type inventories are generally very inadequate; there are many uncertainties in both emission rate and activity extent. For example, the emission inventory for mobile sources should be easy to accurately determine since emission factors can be measured with a dynamometer and activity estimated from vehicle registration and mileage information. When emission factors used for inventories were compared with rates determined by sampling the inlet and outlet concentrations of roadway tunnels, the emission rates for carbon monoxide and hydrocarbons were shown to be twice the levels expected. While CMB can be used to estimate the significance of a source, it requires that the composition of emissions from that source be known. In many cases it is necessary to make an educated guess as to the emission factor and activity level of a source to determine the usefulness of determining a speciation profile of that source.

Samples were analyzed with as much chemical composition detail as possible. The goal was to quantify as many organic compounds as possible that could be used as tracers for a given source. Tracers should be emitted as a stable fraction of the PM, in sufficiently high concentrations to allow measurement in ambient samples, be easily distinguished from other classes of compounds, and be easily quantified. Many types of compounds have been found useful for distinguishing sources. These include polycyclic aromatic hydrocarbons (PAHs), methoxylated phenols, hopanes, steranes, furans, lactones, and sterols. Accompanying inorganic species also must be identified to fully characterize the source profile.

4.0 Source Selection

The sources were selected based on their significance with respect to affecting PM concentrations and the current availability of speciation data. Their significance was determined from either CMB modeling of existing information or from inventory compilation from emission measurements and activity data. Recent studies have shown that the main sources of particulate carbon are mobile sources, residential wood combustion, and meat cooking (Schauer et al., 1996; Watson et al., 1998b).

Existing inventory data are generally compiled as annual averages and do not take into account important parameters such as season, time of day, or meteorology. They are nevertheless a useful starting point and may allow some sources to be considered minor and not useful to profile. Table 4-1 summarizes annual emission rates of the existing source categories for the San Joaquin Valley. Both NO_x and SO_2 can undergo gas-to-particle conversion to PM_{10}, as can a substantial number of the ROG (reactive organic gases) components. Not included in this table are biogenic hydrocarbons, an area source that is difficult to quantify but may be responsible for a significant amount of the annual ROG emissions. The monoterpenes emitted by many of the plant types found in the San Joaquin Valley are easily photooxidized to form particulate matter. However, biogenic emissions are generally at a minimum in the winter due to lower temperature and light intensity.

Table 4-1. Annual Emissions Inventory for the Central California Air Basin (metric tons/day)

Source Type	PM_{10}	NO_x	SO_2	ROG
Geologic	910	37	7	214
Gasoline Motor Vehicle	9	646	24	683
Diesel Mobile Vehicle	24	475	19	102
Burning Vegetation	71	7	0	44
Industrial	105	113	54	398
Natural Gas	83	299	19	32
Aircraft	9	24	2	34

Although this table was a useful starting point, there are significant limitations. For example, PM of geologic origin is by far the greatest source of PM_{10} although its contribution to that fraction is generally much lower under the stagnant conditions under which PM_{10} concentrations are the highest. Burning vegetation is also a seasonal event, much of which is done under conditions that are not stagnant. Many of the other sources have consistent emissions during the year and, therefore, will contribute relatively more during stagnation conditions in the winter.

The primary sources, as outlined in the proposal, consist of the following:

- Gasoline-powered motor vehicles
- Diesel-powered motor vehicles
- Diesel-powered off-road equipment
- Food preparation

- Wood combustion
- Vegetative detritus
- Petroleum production

Geological sources are not included since they generally contain few organic compounds that would be useful as tracers. Motor vehicle sources include tailpipe emissions, brake and tire wear, and entrainment of road dust.

4.1 Existing Source Profiles (with respect to significance, representativeness, and operating conditions)

Table 4-2 summarizes the available information for sources of interest in the San Joaquin Valley. These profiles are limited for several reasons: Proper sampling may not have been done to include semi-volatile organic matter, analytical methods may not have been adequate, or source operating parameters may not be representative of the San Joaquin Valley.

- Gasoline-Powered Motor Vehicles
  Although a large amount of chemical speciation data has been collected for these types of vehicles, relatively few studies have focused on the PM emissions. Fewer yet have resolved the constituents into components that would be useful as tracers. Useful speciation data have been collected by Zielinska et al. (1997, 1998a,b,c), Sagebiel et al. (1996), Norbeck et al. (1998) and Schauer and Cass (2000). The analyses have generally focused on polycyclic aromatic hydrocarbon content of aerosols.

- Diesel-Powered Equipment
  Some speciation profiles suitable for CMB modeling have been previously collected (Zielinska et al., 1997, 1998a, and Abu-Qudais et al., 2001). As with gasoline-powered vehicles, the main focus was on PAH content.

- Cooking Operations
  Speciation profiles from cooking operations have been reported by several investigators (Rogge et al., 1991,1993; Schauer et al., 1999; Zielinska and McDonald, 1999). Most profiles have been collected from charbroiling ground beef. Samples were analyzed for a wide variety of organic species, and alkanoic and alkenoic acids were the most abundant. Cholesterol and γ-lacones were identified as useful tracers.

Table 4-2. Available Information about Sources

	Study	Catagories	Comments
Mobile Sources			
	Zielinski et al., 1997	PAH, hopanes, steranes, and ???	
	Zielinska et a., 1998a	PAH, hopanes, steranes, and ???	
	Sagebiel et al., 1996.	PAH	
	Cadle et al., 1998	?	
	Norbeck et al., 1998	alkanes, alkenes, aromatics, carbonyls, PAH, nitro-PAH, nitrosamines, and dioxins	
Cooking			
	Rogge et al., 1991,1993	Alkanes, alkanoic&alkenoic acids, dicarboxylic acids,alkynals,alkenyls,	
		Ketones, alkenols, furans, lactones, amides, nitriles, PAH, pesticides, and steroids	
	Schauer et al., 1999	n Alkanoic acids, n-alkenoic acids, carbonyls, lactones, alkanes, aromatics, PAHs,	
		alkenes, and steroids	
	Zielinska and McDonald, 1999	PAHs, cholesterol, lactones, carbonyls, alcohols, aromatics, alkananes, and alkenes	
Vegetative Detritus			
	Rogge et al., 1993	n-Alkanes, n-alkanoic&n-alkenoic acids, n-alkanols, n-alkanals, terpenoids	
	Schauer, 1996	?	
Wood Combustion			
	Edye and Richards, 1991	Resin acids ?	
	Ramdahl, 1983	Retene	
	Hawthorne et al., 1988, 1989	Resin acids, methoxylatedphenolics	
	Rogge et al., 1993	Retene, methoxylatedphenolics	
	Rogge et al., 1998	Resin acids	
	Schauer et al., 1996	?	
	McCrillis et al., 1998	PAH	
	McDonald et al., 1998	methoxylatedphenolics and VOC	
	Zielinska et al., 1998a	methoxylatedphenolics and VOC	
	Simoneit et al., 1999	Levoglucosan	
Secondary			
	Gray et al.,1986	OC/EC	
	Turpin, 1991	OC/EC	
Soil and Paved Road			
	Watson, et al., 1997	?	

- Vegetative Detritus
  Rogge et al. (1993) determined profiles of vegetative detritus generated by abrading plant specimens in Teflon bags.

- Wood Combustion
  The organic species composition of wood smoke has been reported by a number of workers. Retene, resin acids, and methoxylated phenols have been identified as useful tracers (Miller et al., 1990; Edye and Richards, 1991; Ramdahl, 1983; Hawthorne et al., 1988, 1989; Standley and Simoneit, 1990; Simoneit et al., 1983; Simoneit and Mazurek, 1982; Rogge et al., 1998; Zielinska et al., 1998c, McDonald et al., 1998, 2000). Methylated phenanthrene compounds (Benner et al., 1995) and levoglucosan (Simoneit, 1998) also have been found to be useful as tracers.

- Petroleum Production
  Petroleum industry combustion sources include heaters, boilers, fluid catalytic cracking unit regenerators, catalytic reforming unit regenerators, sulfur recovery units, stationary IC engines, gas turbines, heater treaters, etc. Most are gas-fired, using either refinery gas, natural gas, or occasionally waste gases. A small number of units are fired with distillate or residual oils, petroleum coke, coal or other petroleum refining byproducts. Those in urban or non-attainment areas such as Los Angeles are almost exclusively gas-fired (England et al., 1998, 2000). Results of direct measurements of organic aerosol emissions from petroleum industry combustion devices are very limited. An estimate of fine carbonaceous aerosol emissions from

major sources in the Los Angeles area based on 1982 data showed that emissions from petroleum industry sources comprise a minor but significant fraction (1.8%) of total emissions (Hildeman et al., 1994b).

Not included are secondary organic sources from chemical reactions in the atmosphere. These usually are complex mixtures in which specific species are not readily identified. In addition, the ROG species may undergo a multitude of reactions that would make identification of the compound released in the source very difficult. Adding to the complexity is that the ambient concentrations may well be a mixture of primary emissions and reaction products.

4.2 Source Profile Chemical Speciation Measurements

The following measurements were made for each source sample. Details of the analytical methods are presented in Section 6.

- Particulate mass by weighing
- Ionorganic elements from x-ray fluorescence (Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr, Y, Zr, Mo, Pd, Ag, Cd, In, Sn, Sb, Ba, La, Au, Hg, Tl, Pb, and U)
- Organic and elemental particulate carbon by thermal/optical reflectance
- Water soluble anions (Cl^-, NO_3,$^-$, $SO_4^=$) by ion chromatography
- Water soluble potassium by atomic absorption spectroscopy
- Ammonium by automated colorimetry
- 160 volatile hydrocarbon species between C_2 and C_{12} by gas chromatography-flame ionization detection
- 99 low volatility hydrocarbons between C_8 and C_{20} by gas chromatography with either flame ionization or Fourier transform infrared/mass spectrometric detection
- 133 semi-volatile organic compounds (polycyclic aromatic hydrocarbons (PAH), methoxylated phenols, hopanes, steranes, lactones, and sterols by gas chromatography-mass spectroscopic detection (GC-MS)
- 14 carbonyl compounds by analysis of 2,4-dinitrophenylhydrazine derivatives by high performance liquid chromatography

4.3 Sources for Profile Data Collection

- On-Road Vehicles
  From previous source-receptor studies, emissions from motor vehicles have been shown to be the major contributor to ambient PM concentrations under stagnant conditions in the winter time (Watson et al., 1998c).

  — Hot Stabilized Mode: This mode is representative of the majority of driving in a typical suburban area. While previous speciation testing has been done, it did not occur under winter conditions with fuels currently used in California.

  — Cold Start: In the first one to two minutes of operation, the catalysts found in gasoline-powered vehicles are not hot enough to significantly reduce emissions. The emissions produced in this operational period are typically equivalent to driving for more than an hour in a hot, stabilized mode. Few chemical speciation data are available for in-use fleets for this mode of operation. Where data are available, the vehicles were not operated under the wintertime condition of the San Joaquin Valley and with California fuels.

  — Visibly Smoking Vehicles: It has been shown that a relatively small percentage of high-emitting vehicles contribute the majority of volatile organic compounds (VOC) emissions from mobile sources (Beaton et al., 1995). Some fraction of these VOCs will be further oxidized in the atmosphere to low-volatility products that will contribute to the PM loading. Visibly smoking vehicles, which are often but not always a subset of high-emitting vehicles, also likely to make a major contribution of PM from this source category. The source profiles from these vehicles have been shown to have composition profiles that are variable between vehicles and significantly different than properly operating vehicles (Watson et al., 1998b).

- Off-Road Diesel Equipment
  In the San Joaquin Valley, off-road diesel power is routinely used in a number of applications such as agricultural operations and construction. Diesels are known to produce significant PM emissions, and the off-road engines are free of any exhaust regulation. In addition, such engines operate under different modes than on-road engines (often at idle or full throttle) and maintenance schedules (often not very rigorous). There is little available information on the chemical composition of PM from these off-road diesel sources.

- Road Dust
  Fugitive PM emissions from roads have been estimated to make major contributions to the PM loading of ambient air. It is likely that these emissions are due to the suspension of debris. The debris consists of material from a variety of sources such as soil, brake and tire wear, vegetative debris, and construction materials.

- Cooking Operations
  Particulate emissions from meat have been shown to be a significant contributor to ambient PM_{10} concentrations. Charbroiling has been shown to be the cooking operation that has the highest PM_{10} emission rate. Fat content has been shown to have the largest effect on the emission rate, perhaps affecting the composition as well. Although CE-CERT has collected much data on the mass of PM emissions from cooking operations, only a few operations have been fully speciated (Zielinska et al., 1998a).

- Petroleum Production
  The production of significant amounts of petroleum in the San Joaquin Valley is unusual for an urban airshed. These emissions are largely fugitive, and their magnitude is difficult to quantify. Although the emissions are largely gaseous, they may contain compounds that are unique for this source and that readily undergo oxidation to less volatile compounds that contribute to the PM loading. A limited composition profile of this source would therefore be useful.

- Wood Combustion
  - Residential Wood: Residential wood burning is likely to be an important contributor to PM during the wintertime episodes in the San Joaquin Valley since wood is mostly likely to be burned during the cool stagnation episodes. PM episodes are also likely to occur during the holiday season when burning for aesthetic reasons is most likely to take place. Commonly used woods are almond, oak, walnut, sycamore, eucalyptus and pine.

  - Agricultural Burns: Agricultural burning is generally not allowed during stagnation episodes and for that reason should not be a major PM contributor. A limited amount of profile data should be collected since the signature from the operations may be unique, and it is likely that such burning might contribute to the background prior to an episode. It is also possible that a significant amount of illegal burning may take place during an episode, especially if it is accompanied by fog. In addition to rice stalks, debris from trimming grapes, almonds, peaches and plums are commonly burned agricultural byproducts.

- Brake Wear
  Although the limited data available suggest that brake wear is not a major contributor to PM in the atmosphere, the source profiles are likely to be sufficiently unique that the source contribution may be detected in the composition of ambient samples. The only recent data on the chemical composition of brake wear was reported by Rogge et al. (1993) and is limited in that the sample was not collected from the aerosol phase, but retrieved from the brake drum of a single late-model truck. The origin of the brake lining was not reported. It should be noted that the speciation of brake wear PM was the subject of 1998 RFP from the California Air Resources Board and that additional data may be forthcoming.

- Tire Wear

  Tire wear previously has been thought to be a minor contributor to ambient PM concentrations. This has been based on the generally large particles that were abraded from tires. Modern radial tires, while they last longer, are also more likely to abrade smaller particles, thus contributing more to PM_{10} concentrations (Cooper, 1996). The only recent data on the chemical composition of tire wear was also reported by Rogge et al. (1993) and is limited in that the sample was not collected from the aerosol phase, but from dust accumulated from a rolling resistance test machine using a single used radial tire. As with brake wear, the speciation was the subject of 1998 RFP from the California Air Resources Board, and additional data may be forthcoming.

5.0 Sample Collection Methodology

5.1 Sample Conditioning

Samples were collected from either ambient or confined air or directly from a source. For directly sampling combustion sources it was necessary to cool and dilute the sample prior to collection for speciation analysis. A DRI-designed a dilution stack sampler was used that was designed to collect fine organic aerosol from combustion sources. The DRI sampler was based on the dilution stack sampler designed and tested at the California Institute of Technology (Hildemann et al., 1989). Figure 5-1 shows a schematic of the DRI version of the dilution tunnel sampler.

Emissions were withdrawn from the stack through heated stainless steel probe followed by a cyclone operating at 113 L/min to remove particles greater than 2.5 μm aerodynamic diameter. The stack gases were transported through a heated stainless steel probe followed by a copper line to the dilution tunnel. In the tunnel the exhaust was mixed with dilution air under turbulent flow conditions to cool and dilute the exhaust to near-ambient conditions. Ambient air filtered through a high-efficiency particulate air (HEPA) filter (to remove particulate matter) and an activated carbon bed (to remove gas-phase organics) was used for dilution. The dilution ratio could be set from 25 to 100-fold dilution. After passing through a tunnel length equal to ~10 tunnel diameters, a fraction of the diluted exhaust entered a large chamber, where additional residence time was provided before the samples are collected. The samples were drawn through a plenum to acquire samples for inorganic and organic speciation. The rest of the diluted exhaust passed through a high-volume sampler filter before being exhausted.

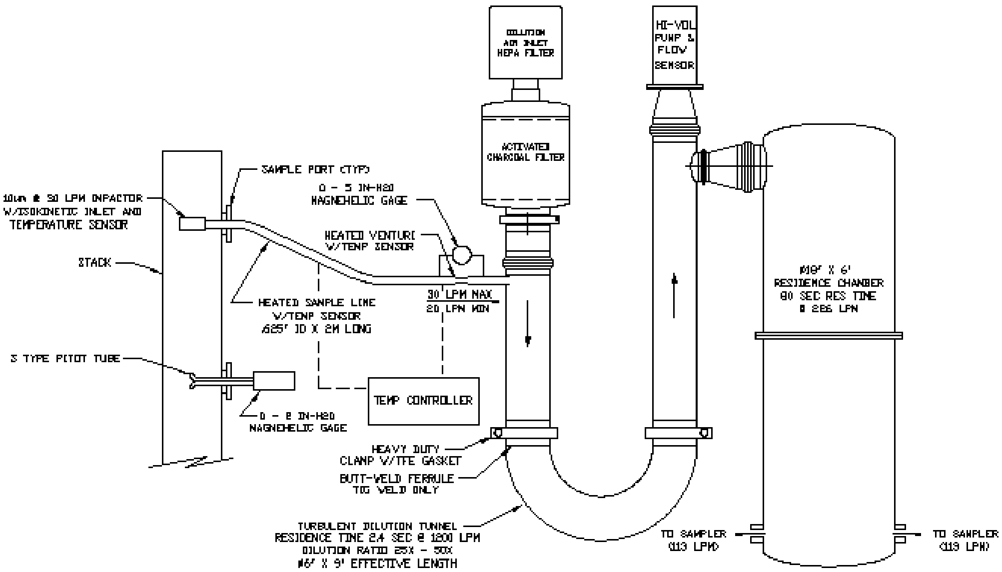


Figure 5-1. Schematic of Desert Research Institute Dilution Tunnel Sampler

Before collecting each source type, the dilution tunnel sampler was vapor degreased. Then the assembled sampler were then wrapped with heat tape and baked at 200 °C for four hours with filtered air flowing through the tunnel. A condensation nuclei counter was used to leak test the sampler after it is assembled on site.

5.2 Sample Collection Processes

- Volatile Hydrocarbons (C_2 to C_{12})
  Stainless steel SUMMA™-polished canisters of 6 L capacity were used for volatile hydrocarbon (C_2-C_{12}) collection. Integrated air samples over the desired time period were collected directly using a stainless steel pump with Viton diaphragm.

- Heavy Hydrocarbons (C_8-C_{20})
  Tenax-TA solid adsorbent was used to collect samples of hydrocarbons containing eight or more carbons.

- Semi-Volatile Organics (SVOC)
  These compounds are distributed between the gas and particulate phases and require special sampling techniques for collection from both phases. Particles larger than 2.5

μm were first be removed with a cyclone sampling at 115 L/min. Teflon-impregnated glass fiber (TIGF) filters were used to collect semi-volatile particulate matter. Volatile components were then be collected with a cartridge containing polyurethane foam (PUF) followed by an XAD-4 (a polystyrene-divinylbenzene resin) followed by a second PUF plug. This sampling approach provided the total SVOC concentration and not the true gas and particle distribution.

- Carbonyl Compounds
  Formaldehyde and other volatile carbonyl compounds were collected, utilizing solid adsorbent cartridges coated with 2,4-dinitrophenylhydrazine (DNPH) reagents, by the method consistent with the EPA document "Technical Assistance Document for Sampling and Analysis of Ozone Precursors" (October 1991, EPA/600-8-91/215). The method is based on the specific reaction of organic carbonyl compounds with DNPH deposited on silica gel or C18 bonded SepPak cartridges in the presence of an acid to form stable derivatives, hydrazones, which are subsequently analyzed by high performance liquid chromatography (HPLC).

- $PM_{2.5}$ Mass and Elements
  Particles larger than 2.5 μm were removed by a perfluoroalkoxy Teflon (PFA)-coated cyclone mounted in a conical PFA-coated plenum. Polyolefin-ringed Teflon filters were used to collect particles for mass and elemental analysis by x-ray fluorescence (XRF).

- $PM_{2.5}$ Carbon and Inorganic Salts
  Quartz filters were used to collect samples for organic and elemental carbon analysis and for water soluble inorganic ions. The sample was collected in parallel with polyolefin-ringed Teflon filter downstream of the cyclone used to remove particles greater than 2.5 μm diameter. The flow rates of the samplers was adjusted to 113 L/min to maintain the cut-point of the cyclone.

5.3 Sampling Procedures

Samples from each source type were collected under operational conditions that were representative of that source as found in the San Joaquin Valley. Table 5-1 summarizes the number and types of samples that were collected. Note that for on-road vehicles samples were collected to augment the sampling being conducted by DRI for a study sponsored by the National Renewable Energy Laboratory (NREL). Sampling procedures were customized for each source. The following describes the procedures that were used.

Table 5-1. Summary of Samples to be Collected and Analyzed

Source	**Description**	**Samples**	**PM Mass**	**XRF**	**IC**	**AA**	**TOR**	**GC-FID***	**DNPH**	**Tenax**	**F/P/X**	Coments
On-Road Vehicles	Low Emitting	15	15*	15*	15*	15*	15*	15	15	15	15*	3 mode collection, unified cycle
	Medium Emitting	15	15*	15*	15*	15*	15*	15	15	15	15*	3 mode collection, unified cycle
	High Emitting	15	15*	15*	15*	15*	15*	15	15	15	15*	3 mode collection, unified cycle
	Smoking	15	15*	15*	15*	15*	15*	15	15	15	15*	3 mode collection, unified cycle
	Replicates	6	6*	6*	6*	6*	6*	6	6	6	6*	3 mode collection, unified cycle
	Blanks	4	4*	4*	4*	4*	4*	4	4	4	4*	
	Heavy Duty Diesel	4	4	4	4	4	4	4	4	4	4	Mobile Diesel system
	Blank	1	1	1	1	1	1	1	1	1	1	Mobile Diesel system
Off-Road Vehicles	Construction Equipment	3	3	3	3	3	3	3	3	3	3	
	Blank	1	1	1	1	1	1	1	1	1	1	
Road Dust	Resuspension Sample	2	2	2	2	2	2				2	
Meat Cooking	Four Types	4	4	4	4	4	4	4	4	4	4	Four cooking types
	Replicates	1	1	1	1	1	1	1	1	1	1	
Petroleum Production		2**	2**	2**	2**	2**	2**	2**	2**	2**	2**	
Wood Combustion	Residential Wood	5	5	5	5	5	5	5	5	5	5	Almond, cedar, eucalyptus, pine,oak
	Agricultural Burning	2	2	2	2	2	2	2	2	2	2	Rice, wheat
	Replicates	2	2	2	2	2	2	2	2	2	2	
Vehicle Wear	Brake	2	2	2	2	2	2	2	2	2	2	
	Tire	2	2	2	2	2	2	2	2	2	2	
	Replicates	1	1	1	1	1	1	1	1	1	1	
Totals (excluding NREL)		100	30	30	30	30	30	98	98	98	30	

* Conducted as a part of the DRI/NREL study
** Conducted as a part of the DRI/GE-EER study
***GC/MS for SI vehicles, GC/FID for the rest of the study

- On-Road Motor Vehicles

  The source composition profiles for gasoline-powered vehicles was developed in cooperation with the gasoline/diesel split study funded by the National Renewable Energy Laboratory (NREL) through the Department of Energy Office of Heavy Vehicle Technologies. The purpose of the NREL study was to determine the contributions of tailpipe emissions from gasoline-powered and diesel-powered motor vehicles to ambient concentrations of $PM_{2.5}$ in the South Coast Air Basin. As part of this study, the Environmental Protection Agency conducted dynamometer tests of light-duty gasoline-powered vehicles and investigators from both the Desert Research Institute and the University of Wisconsin – Madison collected samples for speciation of fine particulate emissions for inorganic and organic species. We leveraged the gasoline/diesel split study by collecting concurrent samples for the remaining volatile organic species specified in the chemical composition profiles for CRPAQS.

  Testing of light-duty vehicles were was conducted by EPA and its contractor, Clean Air Vehicle Technology Center (CAVTC), at the Ralph's Distribution Center in Riverside from June 5 to June 27, 2001. Sixty gasoline-powered motor vehicles in the model year and mileage categories shown in Table 5-2 were tested on the EPA transportable dynamometer using a modified Unified Driving Cycle. Separate samples were collected for each phase of the cycle. Samples for the NREL study include Teflon membrane filters for mass, elements, and ion, quartz filters for organic and elemental carbon by both NISOH and IMPROVE protocols, and TIGF/PUF/XAD for semi-volatile and particulate organic species. The program also included sampling from dilution air and dynamic blanks. A total of 60 composite samples were analyzed (20 sets of vehicles with separate composites for each phase) plus six sets of dynamic blanks. The supplemental samples collected for CRPAQS include canisters for C_2 to C_{11} hydrocarbons, DNPH cartridges for C_1 to C_7 carbonyl compounds, and Tenax cartridges for C_8 to C_{18} hydrocarbons. The canisters were analyzed on-site by gas chromatography with mass spectrometry.

  Table 5-3 shows the protocol for testing the heavy-duty diesel vehicles. Five different cycles were used:

  - City-Suburban Route (CSR)
  - Highway Cycle (HC)
  - Urban Dynamometer Driving Schedule (UDDS)
  - Manhatten Cycle (MC)
  - Idle Cycle.

Table 5-4 describes these cycles used for heavy-duty diesels. The testing was conducted by the West Virginia University Research Corporation in Riverside, CA. Samples were collected using one of the West Virginia University Transportable Heavy-Duty Vehicle Emissions testing laboratories. The test and calibration procedures followed those described in Title 40, Part 86 of the Federal Register when applicable. Testing was conducted using a representative weight. The weight was 70% of the Gross Vehicle Weight Rating (GVWR) up to a maximum of 60,000 pounds. Over the road tractors were assumed to have a GVWR of 80,000 pounds.

Table 5-2. Gasoline Vehicle Testing for the NREL Gasoline/Diesel Split Study

Category	Model Year	Odometer (miles)	Approximate Dates	Number of Vehicle [1]	Number of Composites [2]	Number of Phases	Number of Samples
1	1996 and newer	low mileage (< 50,000)	5,6-Jun	5	1	3	3
2	1993-95	low mileage (< 75,000)	6,7-Jun	5	1	3	3
3	1996 and newer	high mileage (> 100,000)	8,9-Jun	5	1	3	3
4	1990-92	lower mileage (< 100,000)	11,12-Jun	5	1	3	3
5	1993-95	higher mileage (> 125,000)	12,13,14-Jun	8	2	3	6
6	1990-92	> 125,000	14,15,16-Jun	8	2	3	6
7	1986-89	> 125,000	18-19-Jun	6	2	3	6
8	1981-85	> 125,000	19-20-Jun	6	2	3	6
9	1980 and earlier	> 125,000	21-22-Jun	6	2	3	6
10	Smoker	no model year or odometer criteria	25-26-Jun	6	6	3	18
	Total			60	20		60

Table 5-3. Heavy Duty Diesel Vehicle Testing for the NREL Gasoline/Diesel Split Study

Class/Yr Group	GVW Class	Model Year	Cold CSR	Hot CSR	CSR w/Jake	HC	Idle	Cold Idle	UDDS	MC	Dilution Blank	Dynamic Blank
1	I	Pre 90		1		1	1				1	1
2	I	90-93		1		1	1				1	1
3	I	94-97	1	1		1	1				1	
3	I	94-97		1		1	1				1	1
4	I	98-current	1	2		1	1				1	
4	I	98-current		1		1	1				1	
4	I	98-current		1		1	1				1	1
5	II	Pre 90		1		1	1				1	1
6	II	90-93		1		1	1				1	1
7	II	94-97	1	1		1	1				1	
7	II	94-97		1		1	1				1	
7	II	94-97		1		1	1				1	1
8	II	98-current	1	2		1	1				1	
8	II	98-current	1	1		1	1				1	
8	II	98-current		1		1	1				1	1
9	III	Pre 90	1	1		1	1				1	1
9	III	Pre 90	1	1	1	1	1	1	1		2	
10	III	90-93	1	1		1	1				1	
10	III	90-93		1		1	1				1	
10	III	90-93		1		1	1				1	1
11	III	94-97		1		1	1				1	
11	III	94-97		1		1	1				1	
11	III	94-97		1		1	1				1	
11	III	94-97		1		1	1				1	
11	III	94-97		1		1	1				1	1
12	III	98-current	1	1	1	1	1	1	1		2	
12	III	98-current	1	1		1	1				1	
12	III	98-current		1		1	1				1	
12	III	98-current		1		1	1				1	
12	III	98-current		1		1	1				1	1
13	Bus	Electronic		1						1	1	
13	Bus	Manual		1						1	1	
	Total samples collected		10	34	2	30	30	2	2	2	34	12

CSR - City-Suburban Route
HC - Highway Cycle
UDDS - Urban Dynamometer Driving Schedule
MC - Manhattan Cycle

Table 5-4. Test cycles used for heavy-duty diesels

	Cycle				
Parameter	CSR	HC	UDDS	MC	IC
Duration (sec)	1700	1648	1060	1089	
Duration (min)	28.3	27.5	17.7	18.2	
Speed (mph)	16.81	33.96	18.86	6.83	
Distance (miles)	6.68	15.54	5.55	2.07	
Flow (scfm)	1000	1000	1000	1000	
Total diluted volume (scfm)	28333	27467	17667	18150	
Total diluted volume (m^3)	803	778	500	514	
Total diluted volume (m^3) with secondary dilution (10:1 to 45:1) [a]	8026	7781	5005	5142	

[b] Using dilution ratio of 10:1.

CSR - City-Suburban Route
HC - Highway Cycle
UDDS - Urban Dynamometer Driving Schedule
MC - Manhattan Cycle
IC - Idle Cycle

- Off-Road Diesel
  Samples were collected from three representative off-road diesel engines, a 62 HP electrical generator, a 47 HP personal lift or "cherry picker", and a 80 HP backhoe. Typical loads were applied as follows:
  - Generator: It powered the air conditioner at the on-site laboratory.
  - Lift: A 180 pound load was repeatedly raised and lowered.
  - Backhoe: The bucket was filled with 900 pounds of sacked cement ready mix and repeatedly raised and lowered.

  PM and gaseous samples were collected during equipment operation by inserting the inlet probe of the DRI dilution sampling system directly into the exhaust..

- Road Dust
  Two $PM_{2.5}$ samples of road dust were collected in Bakersfield, California using the CE-CERT resuspension sampler. No VOC or SVOC samples were collected since the focus was on the particulate debris on the ropad's surface. The sample location was a closed end roadway cul-de-sac on Charity Ave west of Fruitvale Ave and South of the Rosedale Highway. The traffic at this location was almost exclusively heavy duty Class 8 tanker trucks which were refueling at the refinery. The source areas were half circular areas approximately 10 ft in radius and consisted of approximately 95% asphalt and 5% concrete gutter at the edge of the roadway surface. The vacuum nozzle was slowly moved across the entire surface 3-4 times in a systematic process with at least 10% overlap from each preceding traverse. A TSI DustTrak® was used to measure dust concentrations within the resuspension sampler. The concentrations ranged between 1 and 12 mg/m^3 during the first test and 1 and 96 mg/m^3 for the second. In each case the highest readings were obtained at the asphalt road to concrete gutter interface where the interface created a natural capture area for dirt and

debris. Ambient DustTrak® measurements averaged 140 micrograms/m^3 before and after these tests.

- Cooking Operations

  A total of 12 samples were collected with five types of cooking operations, seven replicates, and three blanks. The types of cooking included:
  - Chicken cooked with charcoal (2)
  - Chicken cooked with a smoker (3)
  - Chicken cooked with an under-fired propane flame (4)
  - Hamburger cooked with charcoal (2)
  - Stir fry chicken and vegetables (1)

  Samples were collected using the DRI sample conditioning system inserted into the hood of CE-CERT's commercial cooking emission test system. The test system also provided the emissions of CO, CO_2, NO_x, PM_{10}, and total hydrocarbons in units of grams/kilogram of product cooked.

- Petroleum Production

  Two source samples were collected from petroleum industry boilers and heaters in the Los Angeles area within the join DRI and GE Energy and Environmental Research Corporation project (funded by DOE). These samples were analyzed for a suit of compounds consistent with CRPAQS list of compounds, without cost to this project.

  An additional sample was collected downwind of the Equilon refinery in Bakersfield at the same location on Charity Avenue that was used for the road dust collection. This location was approximately 700 meters northwest of the refinery across vacant land. The DRI sampler was used for collecting the samples.

- Tire Wear

  Figures 5-1 is a photograph of the apparatus used to generate tire wear. The tire and rim assembly was rotated by a three horsepower electric motor and the tire was forced against a freely-rotating shaft to apply wear force. Both the pressure on the shaft and angle of the tire relative to the shaft were adjusted such that measurable PM sample could be collected with several hours of sampling.

  DustTrak PM_{10} measurements in the vicinity of the contact point between the wheel and roller showed concentrations of 200-400 $\mu g/m^3$ above ambient.

  PM samples were collected using the DRI dilution sampler with the inlet probe mounted under the safety hood that surrounds the test mandrel and coupons. The sampler was operated without dilution air since there is no condensable water being sampled. Two sample sets were collected, one using passenger tires, the other using light truck tires. Each sample consisted of a composite of three types of tires. A background sample of the laboratory air was also collected. To facilitate sample collections, parameters were adjusted to achieve high particulate concentrations, but remain within normal operating conditions. Table 5-5 shows the tires used and the conditions under which samples were collected.

Table 5-5. Tires sampled and operating conditions used.

Tire Brand, Model	Size	Type	Pressure Psi	Load lbs.	Angle deg	Temp deg F	PM Conc. mg/m^3
Goodyear GT+4	225/70 R15	Pass	32		NA	NA	140-210
Goodyear Invicta	225/75 R15	Pass	32		3-5	115-125	210-220
Michelin MX4	P195/65 R15	Pass	32		3-5	120-128	150-160
General Ameriway A/S	235/75 R15	Truck	35		3-5	140-150	141-150
Firestone FR480	P235/75 R15	Truck	35		3-5	130-143	107-120
General Workhorse LT	235/75 R15	Truck	35		3-5	125-135	130-145

Figure 5-1. Apparatus to generate tire wear PM.

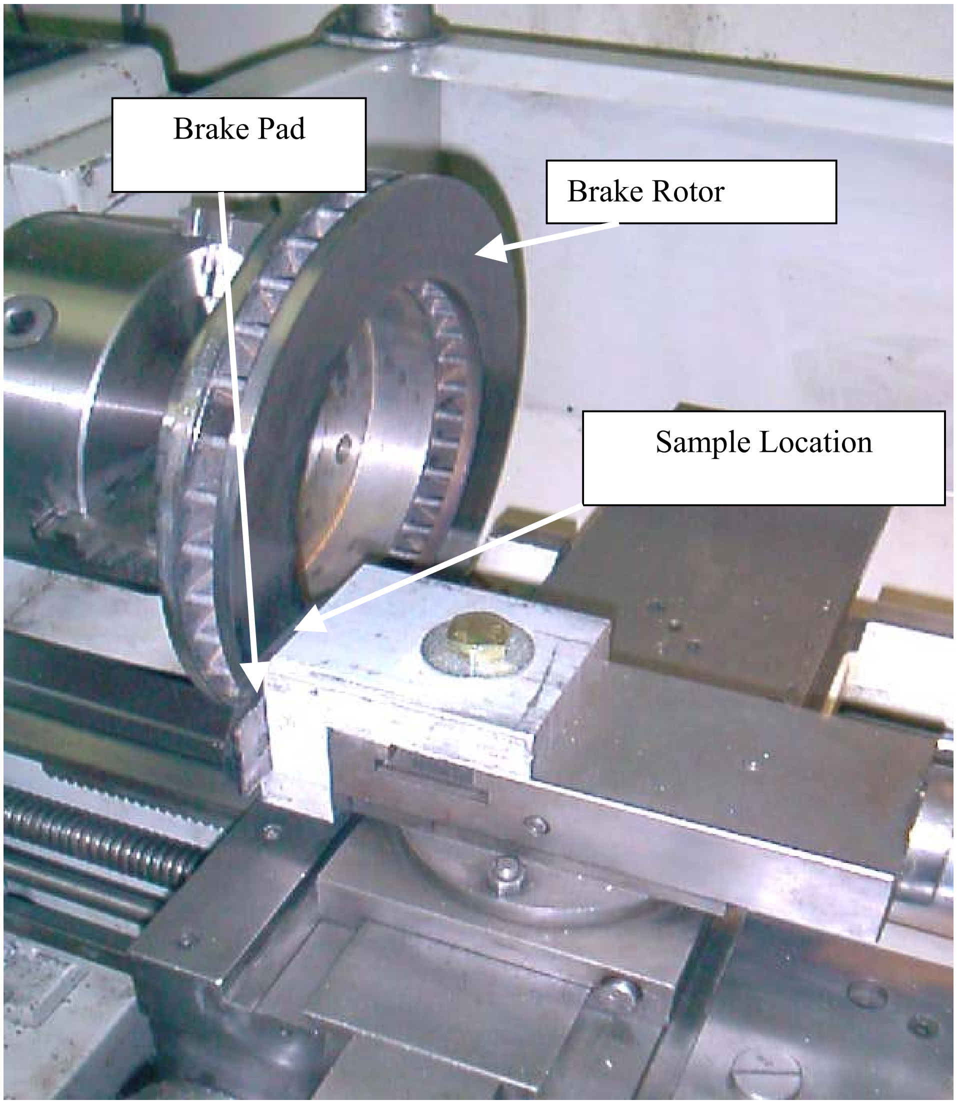
- Brake Wear

The brake wear device was based a lathe on which a rotor was mounted on the rotating shaft and the pads on the tool holder. Pressure between the rotor and pads was regulated by adjusting the horizontal control of the tool holder assembly. Figure 5-2 shows a photo of the device and gives the location at which the sampling probe was placed. An infrared temperature sensor is used to measure the rotor temperature while applying pressure between the pads and rotor. Rotor temperature was measured on several vehicles after heavy braking to determine the realistic temperature to apply. A Thermo Systems Inc. DustTrak® light scattering particulate analyzer was used to determine concentrations of PM_{10} produced in the vicinity of the rotor. Concentrations were approximately ten times higher than ambient when the rotor temperature was brought to 250°C (the maximum observed after heavy braking of a ¾ ton van from 80 mph).

A series of brake pads (organic and metallic) were machined for attachment to the brake fixture that was mounted to the tool holder location. Each brake pad was cleaned with methanol to remove residual solvents or machine oil present from the previous machining operation. Prior to testing each brake pad was partially bedded into the rotor for a period of 5-10 minutes. This process consisted of repeated applications of the brake pad to the rotor until the rotor temperature as measured with an infrared sensor reached at least 250F. Once testing commenced the brake pad was cyclically applied to the rotor. Rotor temperature was periodically checked to maintain operation in the range of 250 to 400F. The DustTrak® was used to qualitatively assess the emission rate and to provide a consistent stream for the sample system.

Organic pads had a higher coefficient of friction as compared to the metallic compound brakes. This resulted in significantly higher rotor temperatures to achieve the same mass emission rate as measured by the infrared thermometer. Each brake sample was tested for a total of 20 minutes and exchanged for each of the other pads until the sequence of 3 metallic and 3 organic pads were collected. A replicate metallic pad sample was also collected.

Figure 5-2. Apparatus for generating brake wear PM.



- Residential Wood Burning
  Residential wood smoke was generated using a commercial wood-burning fireplace. Five samples were collected, one each for almond, cedar, pine, oak and eucalyptus purchased in the Fresno area. A replicate oak and cedar samples were collected. Samples were collected using the DRI dilution tunnel and sampler. The fires were started with 0.5 kg kindling underneath 5 kg wood and ignited with a propane torch. After the kindling was completely burned, the sampling was started. The fire was then recharged with 5 kg of wood after approximately 30% of the original load has burned to maintain a vigorous flame (but not so vigorous as to extend into the flue) throughout the sampling period. The DRI sampler was used to collect all samples using a diluting a factor of twenty using air passed through activated charcoal followed by a HEPA filter. Samples were collected over a four hour period.

- Agricultural Burning
  Two samples of rice stubble and one of wheat were burned in the commercial wood-burning fireplace. The DRI sampler was used to collect sample from ignition until the residue no longer is observed to smolder.

- Brush Fire Burning
  Although not included in the Work Plan, we used the opportunity of a brush fire near the DRI laboratory to collect samples using the DRI sampler without dilution. Two samples were collected for VOC and carbonyl analysis and six for SVOC analysis.

6.0 Sample Analysis Methodology

The following analytical methods were used:

- Gravimetric Analysis
  A Metlet MT5 electromicrobalance was used to weigh Teflon membrane filters to the nearest microgram (μg) before and after sampling. All substrates were conditioned at 21.5 +/- 1 °C and 35 +/- 5% RH for at least 24 hours prior to weighing and had electrical charges removed with a Polonium^{210} radiation source immediately prior to weighing.

- X-ray Fluorescence Measurement for Elemental Composition
  A Kevex Corporation model 700/8000 energy dispersive x-ray fluorescence analyzer was used to measure the concentrations of Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr, Y, Zr, Mo, Pd, Ag, Cd, In, Sn, Sb, Ba, La, Au, Hg, Tl, Pb, and U on Teflon membrane filters.

- Thermal/Optical Reflectance Carbon Analysis

Sections of quartz fiber filter substrates were analyzed by thermal volatilization in seven progressive temperatures and two purge gases:

- ambient to 120 °C under helium
- 120-250 °C under helium
- 250-450 °C under helium
- 450-550 °C under helium
- 550 °C under 98% helium/2% oxygen mixture
- 550-700 °C under the helium/oxygen mixture
- 700-800 °C under the helium/oxygen mixture

The volatilized carbon was converted to CO_2 by heated manganese dioxide, reduced to methane with a nickel catalyst, and quantified as methane with a flame ionization detector. An optical system was used to correct for pyrolysis during the temperature treatment. This temperature/concentration profiling was used to characterize the nature of the carbon in the sample by volatility (Chow et al., 1993). The minimum detection limit (MDL) is approximately 12 μg of TC per 47 mm quartz filter.

- Ion Chromatographic Analysis for Chloride, Nitrate, and Sulfate
  Sections of quartz filter substrates were extracted by shaking followed by sonication in de-ionized water. The concentrations of CL-, NO_3-, and $SO_4^=$ in the solution were determined by Dionex model 2020i ion chromatograph.

- Automated Colorimetric Analysis for Ammonium
  Ammonium in the water extract from quartz filters was determined by a Technicon model TRAACS 800 Automated Colorimetric System. The analysis was based on the reaction of ammonium with phenol and sodium hypochlorite to produce indolphenol. Potential interferents included formaldehyde, hydrogen sulfide, nitrate, and sulfate. The MDL was approximately 0.33 μg of ammonium per 47 mm quartz filter.

- Atomic Absorption Spectrometric Analysis for Water-Soluble Potassium
  Potassium in the water extract from the quartz filters was determined by a Varian model 880 Double Beam Atomic Absorption spectrometer. The absorption feature at 766.5 nm was used. The MDL was approximately 0.05 μg potassium per 47 mm quartz filter.

- Gas Chromatographic-Flame Ionization Detection Measurement of C_2-C_{12} Hydrocarbons
  Hydrocarbons in the air from the sampling canister were concentrated in a freeze-out trap immersed in liquid oxygen. The contents of the trap were then immersed in boiling water and injected into a Hewlett-Packard model 5890 series II gas chromatograph equipped with either a J&W DB-1 fused silica capillary column(for compounds > C_4) or a J&W GS-Alumina PLOT fused silica capillary column (for C_2 to C_4 compounds) and a flame ionization detector or mass spectrophotometric detector. Up to 160 compounds were identified by retention time with a lower quantifiable limit of 0.1 ppbC.

- Gas Chromatographic-Flame Ionization Detection Measurement of Low Volatility Hydrocarbons
  Samples collected for low volatility hydrocarbon analysis on Tenax adsorbent tubes were desorbed with a Chromepack Thermal Desorption-Cold Trap Injection (TCT). The volatilized carbon was then separated into components by a gas chromatograph equipped with a J&W DB-1 fused silica capillary column and either a Fourier transform infrared/mass spectrophotometric (IRD/MSD) or flame ionization (FID) detector. This technique can identify up to 99 individual compounds with a sensitivity 0.02-0.05 μg.

- Gas Chromatographic-Mass Spectral Detection of Semi-Volatile Organic Compounds
  Samples collected for low and semi-volatile organic analysis on the PUF/XAD/PUF cartridges and TIGF filters were extracted with solvents. PUF substrates were first Soxlet-extracted with a 10/90 mixture of diethyl ether/hexane and then by acetone. The XAD and TIGF substrates were first microwave-extracted with dichloromethane and then acetone. The solutions were combined, the solvent removed and the residue dissolved in acetonitrile. This solution was then analyzed by as follows:
  — Polycyclic aromatic hydrocarbons (PAH), hopanes, sterenes, and alkanes: An electron impact (EI) GC/MS technique, using a Varian CP-3800 gas chromatograph equipped with a 8200 CX Autosampler and interfaced to a Varian Saturn 2000 Ion Trap Mass Spectrometer or Varian CP-3400 gas chromatograph with a model CP-8400 Autosampler and interfaced to a Saturn 2000 Ion Trap Mass Spectrometer. Injections are 1 μl in size in the splitless mode onto a 30m long 5% phenylmethylsilicone fused silica capillary column (J&W Scientific type DB-5): CP-Sil8 Chrompack (30m x 0.25mm x 0.25 mm) for PAH, hopanes and steranes, and alkanes.
  — Organic acids, methoxylated phenol derivatives, cholesterol, sitosterol, and levoglucosan: Analyzed together by GC-MS after derivitization to TMS esters and ethers by BSTFA (bis(trimethylsilyl)trifluoroacetamide) using isobutane chemical ionization, using a Varian CP-3800 gas chromatograph equipped with a 8200 CX Autosampler and interfaced to a Varian Saturn 2000 Ion Trap Mass Spectrometer or Varian CP-3400 gas chromatograph with a model CP-8400 Autosampler and interfaced to a Saturn 2000 Ion Trap Mass Spectrometer. Injections are 1 μl in size in the splitless mode onto a 30m long 5% phenylmethylsilicone fused silica capillary column (J&W Scientific type DB-5): CP-Sil8 Chrompack (30m x 0.25mm x 0.25 mm).

The typical sensitivity of these SVOC methods was 0.02-0.05 μg/sample.

- HPLC Analysis of Carbonyl Derivatives
  Samples collected on cartridges coated with 2,4-dinitrophenylhydrazine were extracted in acetonitrile and the extract hydrozone content was analyzed using a Waters HPLC with UV detection at 360nm. The concentrations of 14 aldehydes and ketones were reported. The MDL was approximately 0.1 ppbv of carbonyl compound for 180 L of sample collected.

7.0 Quality Assurance/Quality Control

Quality assurance consisted of:

- Organizational responsibility.
- Maintaining standard operating procedures (SOPs) for sample collection, analysis, data validation, and data presentation.
- Specifying the data quality objectives.
- External audits.

Quality control consisted of:

- Following SOPs for sample collection, sample custody, analysis, data validation, and data presentation.
- Collection and analysis of replicate samples.
- Implementation of quality control steps in the SOPs such as calibration interval, replicate samples, and blank variability.
- Equipment maintenance.
- Acceptance testing.
- Operator training.
- Supervision.
- Management support.

8.0 Data Management

All data were subjected to Level 1A data validation as specified by Watson et al. (1998a). For this validation data were removed for periods in which instruments malfunctioned or did not meet quality control specifications. Data were adjusted for span or interference biases. Outliers are checked against other measurements for consistency and flagged if they are not.

All data were submitted as EXCEL spreadsheets.

9.0 Results

Table 9-1 summarizes the data that were collected. All samples were collected as stated in the Work Plan and in several cases additional samples were collected. The only analyses that were invalidated were the TENAX samples collected for wood combustion. These were invalidated due a leak in the sampling system. Samples for inorganic analyses were not collected for the wildfires. Due to the vast amount of data it is not practical to include the data in the hard copy version of this report. The data are submitted as EXCEL appendices in the electronic version of this report as the following workbooks:

- Final Data Off-Road, Road Dust, Brake&Tire.xls

- Final Data On-RoadR.xls
- Final Data Wood Combustion
- Final Data Meat Cooking.xls

Table 9-2 summarizes the location of the data and the units. Data collected under the separate DRI-NREL and DRI-GE-EER studies have not yet been approved for release and are so noted in the tables. Once released, the tables will be updated to include this data.

Table 9-1. Summary of samples collected and analyzed compared with proposed (#proposed/#completed)

Source	Description	Samples	PM Mass	XRF	IC	AC	AA	TOR	VOC***	Tenax	F/P/X	DNPH
On-Road Vehicles	Low Emitting	15/	15/	15/	15/	15/	15/	15/	15/	15/	15*/ 0	15/
	Medium Emitting	15/	15/	15/	15/	15/	15/	15/	15/	15/	15*/ 0	15/
	High Emitting	15/	15/	15/	15/	15/	15/	15/	15/	15/	15*/ 0	15/
	Smoking	15/	15/	15/	15/	15/	15/	15/	15/	15/	15*/ 0	15/
	Replicates	6/	6/	6/	6/	6/	6/	6/	6/	6/	6*/ 0	6/
	Blanks	4/	4/	4/	4/	4/	4/	4/	4/	4/	4*/ 0	4/
	Heavy Duty Diesel	4/	4/	4/	4/	4/	4/	4/	4/	4/	4*/ 0	4/
	Blank	1/	1/	1/	1/	1/	1/	1/	1/	1/	1*/ 0	1/
	Total Analyzed	**296**	**296**	**296**	**296**	**296**	**296**	**296**	**122**	**72**	**NA**	**117**
Off-Road Vehicles	Construction Equipment	3/ 6	3/ 6	3/ 6	3/ 6	3/ 6	3/ 6	3/ 6	3/ 7	3/ 6	3/ 6	3/ 7
	Blank	1/ 2	1/ 2	1/ 2	1/ 2	1/ 2	1/ 2	1/ 2	1/ 2	1/ 2	1/ 2	1/ 2
Road Dust	Resuspension Sample	2/ 2	2/ 2	2/ 2	2/ 2	2/ 2	2/ 2	2/ 2	0/ 0	0/ 0	0/ 0	0/ 0
Meat Cooking	Five Types	5 5	5 5	5 5	5 5	5 5	5 5	5 5	5 4	5 5	5 5	5 5
	Replicates	1/ 7	1/ 7	1/ 7	1/ 7	1/ 7	1/ 7	1/ 7	1/ 1	1/ 6	1/ 6	1/ 6
	Blanks	0/ 3	0/ 3	0/ 3	0/ 3	0/ 3	0/ 3	0/ 3	0/ 0	0/ 1	0/ 1	0/ 1
Petroleum Production		2**/ 0	2**/ 0	2**/ 0	2**/ 0	2**/ 0	2**/ 0	2**/ 0	2**/ 0	2**/ 0	2**/ 0	2**/ 0
	Equilon Refinery	0/ 1	0/ 1	0/ 1	0/ 1	0/ 1	0/ 1	0/ 1	0/ 1	0/ 1	0/ 1	0/ 1
Wood Combustion	Residential Wood	5/ 5	5/ 5	2 5	5/ 5	5/ 5	5/ 5	5/ 5	5/ 5	5/ IV	5/ 5	5/ 5
	Agricultural Burning	2/ 2	2/ 2	2/ 2	2/ 2	2/ 2	2/ 2	2/ 2	2/ 2	2/ IV	2/ 2	2/ 2
	Wild Fires	0/ varies	0/ 0	0/ 0	0/ 0	0/ 0	0/ 0	0/ 0	0/ 2	0/ IV	0/ 6	0/ 2
	Replicates	2/ 3	2/ 3	2/ 3	2/ 3	2/ 3	2/ 3	2/ 3	2/ 3	2/ IV	2/ 1	2/ 2
Vehicle Wear	Brake	2/ 2	2/ 2	2/ 2	2/ 2	2/ 2	2/ 2	2/ 2	2/ 2	2/ 3	2/ 3	2/ 3
	Tire	2/ 2	2/ 2	2/ 2	2/ 2	2/ 2	2/ 2	2/ 2	2/ 2	2/ 2	2/ 2	2/ 2
	Replicates	1/ 1	1/ 1	1/ 1	1/ 1	1/ 1	1/ 1	1/ 1	1/ 1	1/ 1	1/ 1	1/ 1
	Blank	0/ 1	0/ 1	0/ 1	0/ 1	0/ 1	0/ 1	0/ 1	0/ 1	0/ 1	0/ 1	0/ 1
Totals (excluding NREL)		100/ 337	30/ 41	30/ 337	30/ 337	30/ 337	30/ 337	30/ 337	98/ 154	98/ 99	30/ 41	98/ 156

*** Conducted as a part of the DRI/NREL study (currently not available)**
**** Conducted as a part of the DRI/GE-EER study**
*****GC/MS for on-road vehicles, GC/FID for the rest of the study**
NA = Not Available
IV = Invalidated

Table 9-2 Location of data within worksheets and units used.

Measurement Method	Species	Worksheet	Units	Comments
Gravimetric	PM mass	TOR & Inorganics	μg/m^3	
XRF	38 Elements Al-U	TOR & Inorganics	μg/m^3	
Thermal/Optical Reflectance	Elemental and Organic Carbon	TOR & Inorganics	μg/m^3	4 OC & 3 EC Thermal fractions
Ion Chromatography	Cl^-, NO_3^-, SO_4^{-2}	TOR & Inorganics	μg/m^3	
Automated Colorimetric	NH_4^+	TOR & Inorganics	μg/m^3	
Atomic Absorption	K^+	TOR & Inorganics	μg/m^3	Water soluable
GCFID-VOC	116 C_2-C_{12}	VOC	ppbC	
GCFID-Tenax	39 Hydrocarbons	Tenax	μg/m^3	
Semi-Vol GCMS	PAHs	PAH	ng/m^3	
Semi-Vol GCMS	Hopanes and Steranes	Hop&Ster	ng/m^3	
Semi-Vol GCMS	Heavy Alkanes	Hearvy Alkane	ng/m^3	
GCMS-esterification	Organic Acids	Polar VOC	ng/m^3	
HPLC-hydrazones	14 Aldehydes & Ketones	HPLC	ppb/μg/m^3	Units are indicated in worksheet

10.0 References

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